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13. ABSTRACT (Maximum 200 words)

Our work has led to 1) the identification of several new and facile routes to preparing polyphenylene and poly(arylene vinylene)-type polymers and copolymers, 2) the development of highly-efficient organolanthanide complexes and dendrimers for both photon and excited-state energy harvesting, 3) the demonstration of triplet excited-state harvesting and electrophosphorescence in polymers used for light-emitting diodes, and 4) the development of two-photon active dyes for chemical sensing and photonic applications. It is expected that these four accomplishments will lead to more robust and efficient polymers for solar energy harvesting and light-emitting devices, as well as optical sensors for the detection of chemicals and biological agents.

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Sincerely,

Aaron W. Harper

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

I. New Syntheses of Poly(arylene vinylene)-Type Conjugated Polymers

Three new reactions have been developed for the preparation of poly(arylene vinylene)s. The first reaction involved an acyclic diene metathesis (ADMET) polymerization of 2,5-dialkoxy-1,4-divinylbenzenes to produce the corresponding poly(phenylene vinylene) (PPV) in excellent yield. Furthermore, the polymers produced by this method were of high molecular weight, and were free of contaminants. This method is of general applicability to the polymerization of a wide variety of divinylbenzene monomers. The second reaction involves the reaction of sodium diethylphosphite on aromatic dialdehydes to produce the target poly(arylene vinylene). For example, the polymerization of 2,5-dioctyl-1,4-terephthaldehyde to the corresponding (PPV) proceeded under mild conditions and in high yield. The third reaction is the direct oxidation of bis-Wittig salts (e.g. 2,5-didecyloxy-α,α'-xylylbisphosphonium bromide) directly to the PPV polymer. In a one-pot, two-step reaction, the bis-Wittig salt is first deprotonated to form the diylide. Treatment of this intermediate with one half equivalent of elemental sulfur produces a transient thioaldehyde, which reacts with the remaining ylide moiety to produce the vinylene linkage. Advantages of this method are that comonomers are not necessary (so that low molecular weights due to stoichiometric imbalance is not an issue), ease of synthesis of the polymer, and that carbonyl defects are not possible (carbonyl groups are known to quench the excited states in PPVs). Advantages of these three new synthetic routes over traditional routes to poly(arylene vinylene)s include ease of synthesis, ready availability of starting materials, high reaction yields, high molecular weights, and low concentrations of contaminants.

II. Design and Syntheses of Highly-Luminescent Organolanthanides for Triplet Exciton Harvesting, and Syntheses of PPP-Type Host Matrix Polymers

In addition to developing reactions to prepare the necessary block copolymers, we have made considerable progress in preparing highly efficient organolanthanide complexes, which are integral components of the light-harvesting block copolymers. We have developed a new class of organolanthanides that employ 4-acylisoxazolone and 4-acylpyrazolone ligands. These new ligands aromatize upon lanthanide binding, and thus result in the creation of a pi-system manifold with which to photosensitize the lanthanide ion by nonradiative energy transfer. Furthermore, these ligands are extremely versatile in their chemical design, from which adequate steric bulk can be incorporated to ensure the prevention of concentration quenching. Also, we have synthesized some of these ligands that are devoid of C-H bonds, and result in organolanthanides with enhanced quantum yields of emission and extended excited state lifetimes. This has important implications in optical signal amplification and organic solid-state lasers. One example of these compounds is shown in Figure 1.

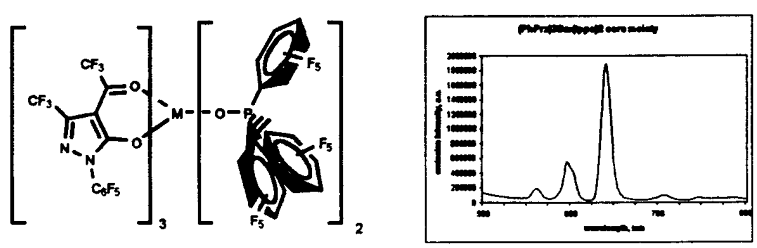


Figure 1. A europium chelate with 4-acylpyrazolone ligands. Note that there are no C-H bonds in the molecule. Also shown is the associated emission spectrum when excited into the pyrazole $\pi-\pi^*$ transition.

We have also incorporated organolanthanides in conjugated polymers to harvest triplet excited states for light production. One major problem with traditional photo- and electroluminescent polymers is that three out

of four excited states that are generated are triplet, and do not lead to emission. By transferring the triplet excited state energy to a luminescent lanthanide, all excited-state energy in the material can result in the production of light, leading to a brighter and more efficient device. We have doped the conjugated polymer poly(2-benzoyl-1,4-phenylene) with various organolanthanides and have shown emission from the lanthanides that could only come from triplet energy harvesting from the polymer. An example is shown in Figure 2.

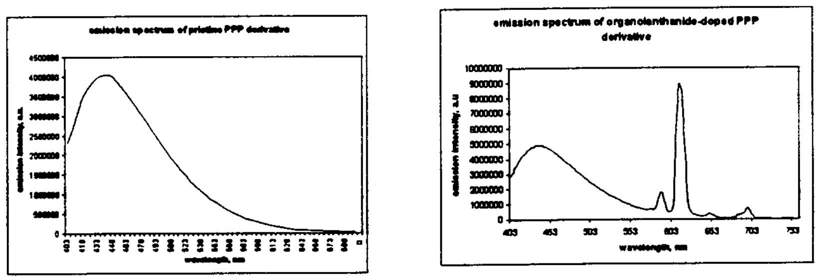


Figure 2. Left: Emission spectrum of the pristine PPP polymer (in $CHCl_3$), showing singlet emission. Right: Emission spectrum of the same polymer doped with $(hfa)_3Eu$, showing both singlet emission and lanthanide emission arising from triplet photosensitization. ($(hfa)_3Eu$ is incapable of emission by direct excitation).

The polymers that we have developed as host matrices for these organolanthanides are of the polyphenylene type. These polymers are shown below. At the time of this report, these polymers have only been characterized for their polymer properties (i.e. molecular weight, polydispersity, chemical characterization such as NMR spectroscopy, etc.).

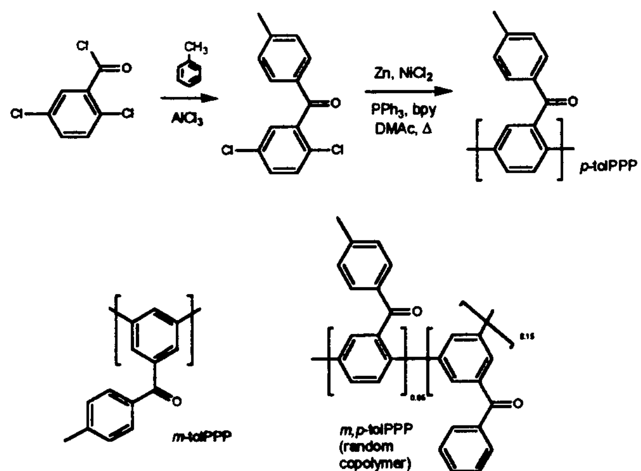
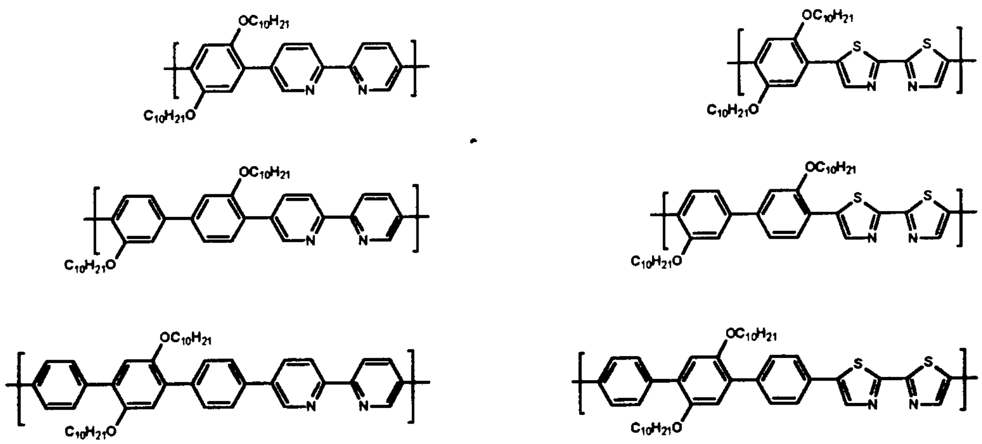


Figure 3. PPP-type polymers that have been developed as host matrices for our organolanthanides.

We have continued along these lines by not only designing appropriate organolanthanide dopants for other conjugated polymers, but are also covalently incorporating organolanthanides as integral components of conjugated polymers. The idea here is to attach the lanthanides to the polymer in such a way as to incorporate the lanthanide into the pi-system of the polymer. The energy transfer is expected to be facilitated by intermolecular energy transfer and/or Dexter energy transfer, either in addition to, or instead of, Forster energy transfer. Furthermore, it is expected that by incorporating the lanthanide into the wavefunction of the polymer pi-system, the lanthanide will exert a heavy-atom effect and help to transmute the singlet excited states to triplet excited states, which can then be harvested by the lanthanide. To date, progress in the preparation of various monomers has been achieved, and include the following (the target polymers are shown as well):

target polymers (to which organolanthanides will be attached at the diimine moieties):



monomers prepared to date:

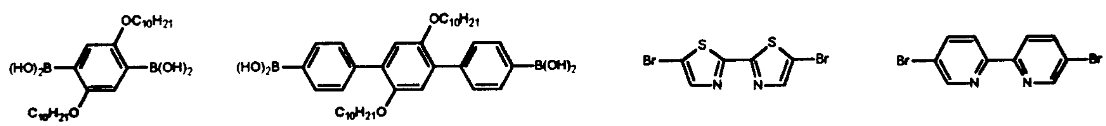


Figure 4. Target chelating polymers and the constituent monomers prepared to date. A systematic decrease in triplet energies of the polymers is expected as one goes from phenyl to biphenyl to terphenyl moieties.

III. Design and Syntheses of One- and Two-Photon Chemical Sensors

Over the past year, we have also developed chemically-responsive molecules for the detection of chemical agents. Molecules have been prepared that possess two large internal transition dipole moments as well as a binding site for a desired analyte. Complexation with an analyte results in large conformational and electronic perturbations to the molecule, which leads to a pronounced shift in both the absorption and emission bands of the compounds. One such example is shown in Figure 5. In the pristine state (i.e. no analyte present), the internal dipoles cancel, and the compound is yellow, with a blue fluorescence. However, upon binding of a proton or metal cation, the components of the internal dipoles become additive, leading to a pronounced red-shift in both the absorption and emission spectra. Thus, upon addition of an acid to a solution containing the chemosensor, the solution becomes a deep red color, and is red fluorescent under ultraviolet excitation. We are presently exploring the use of these and similar molecules for use as colorimetric and fluorimetric chemosensors.

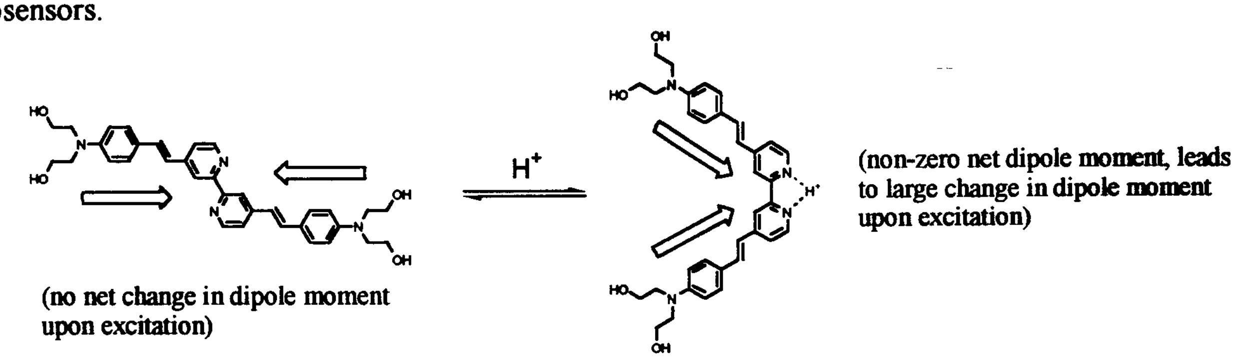


Figure 5. An example of a simultaneous one- and two-photon chemosensor. The molecule has been designed to have a large change in internal quadupole and dipole moment upon binding of an analyte. These changes lead to very large shifts in both the absorption and emission spectra of the molecule.

We are also aware that these compounds are in essence quadrupolar two-photon chromophores, and are currently exploring the use of these compounds not only as new two-photon molecules, but also as two-photon chemosensors. Two-photon chemosensors is a wholly new concept that has never before been explored. We

are presently developing two-photon chemosensors for use in chemical, biological, and environmental detection of analytes, where advantages of two-photon phenomena (i.e. greater depth penetration, small-volume localization, suppression of autofluorescence) can be fully exploited, and offers unique opportunities over one-photon-based chemosensors.

To date, we have prepared the following series of two-photon molecules:

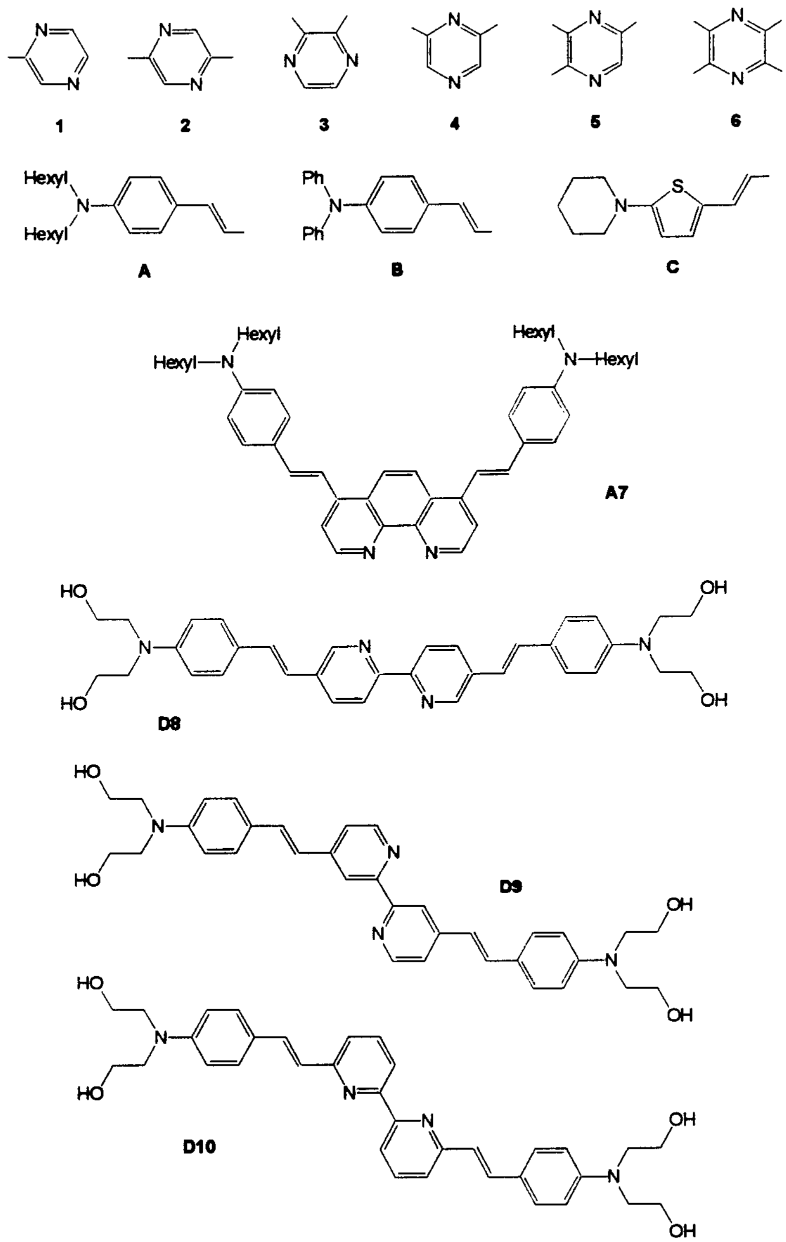


Figure 5. Two-photon molecules prepared to date. In the top of the figure, molecules A1-A6, B1-B6, and C1-C6 are constructed by attaching A, B, C to each dangling bond(s) of components 1 through 6. The molecules are similar to those of D8-D10.

These molecules have been characterized in terms of their absorption spectra and one-photon excitation and emission spectra. It has been determined that very complex photophysics occurs in these molecules, owing to the presence of multiple chromophores existing in each molecule. Thus, intramolecular energy transfer occurs, which complicates a complete understanding of the photophysical nature of these molecules. Future work involves a detailed time-resolved emission study of these molecules, as well as their two-photon photophysical characterization. Their response to chemical analytes (i.e. acids, Lewis acids, metal ions) is to be explored, as well.

Other Relevant Items:

List of papers presented at meetings, but not published in conference proceedings

"Supramolecular Interactions in Electro-Optic Polymers," invited presentation (and first speaker) at the 23rd Asilomar Conference on Polymers, Pacific Grove, CA, 2/6/00.

"Syntheses and Application of Organolanthanides in Photonics," invited presentation, Joint Southeast/Southwest Regional American Chemical Society annual meeting, December, 2000.

List of papers presented at non-conference venues

"Supramolecular Interactions in Nonlinear Optical Polymers," invited presentation, University of Wisconsin – River Falls, River Falls, WI, 2/18/00.

"Fun with Photons: A Lighthearted Look at a Research Career," invited presentation, University of Wisconsin – River Falls, River Falls, WI, 2/19/00.

"Supramolecular Interactions in Electro-Optic Polymers," invited presentation, University of North Texas, Denton, TX, 4/14/00.

Scientific Personnel supported by this project

Aaron W. Harper, PI
Jeremy C.Collette, graduate student (Ph.D. track)
Cory Miller, graduate student (Ph.D. track)
Asanga Padmaperuma, graduate student (Ph.D. track)

Honors and Awards received within this report period

Beckman Young Investigator Award (Harper)
Presidential Early Career Award for Scientists and Engineers (Harper)